DRIP OIL DISTILLATES
BOILING POINT ABOVE 110° CENTIGRADE

BY

N. ISENBERG

W. C. LUCKOW

ARMOUR INSTITUTE OF TECHNOLOGY

1 9 1 6

665
L 96

Illinois Institute
of Technology
UNIVERSITY LIBRARIES

AT 416
Isenberg, N.
Drip oil distillates boiling
point above 110 Centigrade

For Use In Library Only

DRIP OIL DISTILLATES

BOILING POINT ABOVE 110° CENTIGRADE

A Thesis

Presented by

NATHAN ISENBERG

and

WILLIAM CHARLES LUCKOW

to the

PRESIDENT AND FACULTY

of the

ARMOUR INSTITUTE OF TECHNOLOGY

For the Degree of

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

Having Completed the Prescribed

Course of Study

in

Chemical Engineering

1916

Approved:

Harry McCormack
Prof. of Chemical Engineering

H M Raymond
Dean of Engineering Studies

Dean of Cultural Studies

ILLINOIS INSTITUTE OF TECHNOLOGY
PAUL V. GALVIN LIBRARY
35 WEST 33RD STREET
CHICAGO, IL 60616

DRIP OIL DISTILLATES

Boiling Point

Above 110°C.

by

NATHAN ISENBERG

and

WM. CHARLES LUCKOW

26438

TABLE OF CONTENTS.

Introduction........................Page 1
Material Investigated................... 2
Method of Attack........................ 3
Primary Distillation.................... 5
    Apparatus Used...................... 5
    First primary distillation.......... 6
    Second primary distillation......... 8
    Difficulties Encountered............10
Fractional Distillation.................11
    Theory..............................11
    Apparatus used. 14
    Procedure...........................15
Identification of the Hydrocarbons......20
    Methods of procedure................
Conclusion..............................34
Bibliography............................35

Acknowledgement

We are greatly indebted to Professor H. McCormack and to Associate Professor B. B. Freud for their kindly interest and helpful suggestions throughout the course of this work.

I.

Introduction.

Very recently it was found that drip oil, a condensate pumped from the collecting sumps in the city gas mains, contains a considerable amount of benzol and toluol which may be recovered by distillation in a column still. After these products have been removed, a large residue remains which supposedly contains the higher homologues of benzene.

The object of this study of drip oil distillates was to prove the presence of these higher homologues of benzene, with special reference to the dimethylbenzenes (xylenes) and the trimethylbenzenes (cumene, pseudocumene, and mesitylene), which find their application as the basis of many organic dyes.

To the best of our knowledge we are the first to undertake an investigation of drip oil distillates with boiling points above 110°C. For this reason we were unable to find any specific information in the literature.

Material Investigated.

The drip oil used for this work was obtained from the Gas Oil Company, which is situated at Hammond, Indiana. The original material, as obtained by this company, was probably a composite material obtained from plants making water gas and plants making coal gas. This material was treated with 2% by weight of concentrated sulphuric acid and distilled up to a temperature of 135°C. We received the residue from this distillation, called the drip oil "tailings."

The material was a thick, black, tarry liquid, having a characteristic odor.

Method of Attack.

In order to determine the nature of an unknown substance, whether liquid or solid, we must first purify it (remove sulphur compounds, unsaturated compounds, etc.). This is generally accomplished by washing with concentrated sulphuric acid and removing the sludge formed.

The material is then ready for a primary distillation. The cuts are made according to the nature of the distillate, namely, as to quantity, color, and state, i.e., solid or liquid. These fractions are then treated with Fuller's-earth in order to remove small amounts of water, which generally causes turbidity of the fraction, and also to remove any obnoxious odors.

The clear fractions are now ready for the process of fractional distillation. The object

of the process of fractional distillation is to obtain fractions which have a constant boiling point. This end is only attained on repeated fractional distillation. We have noted instances in the literature where as much as sixteen months of continuous fractional distillation were required before constant boiling fractions were obtained.

Having obtained the constant boiling fractions we are in a position to identify them. To accomplish this, there are several methods of attack. One method is to determine the molecular weight by vapor density measurements. Another method is by sulphonation or nitration, by which means a body of definite melting point can be obtained.

Primary Distillation.

Apparatus Used:-

The apparatus, shown in figure 1, consists of, (a) an iron still with a capacity of about eight liters, which is provided with a tightly fitting top. This top is provided with a vapor neck and a stuffing box for the thermometer. (b) A condenser, which consists of a long metal condenser tube inserted into a glass tube. (c) The receivers used were of glass.

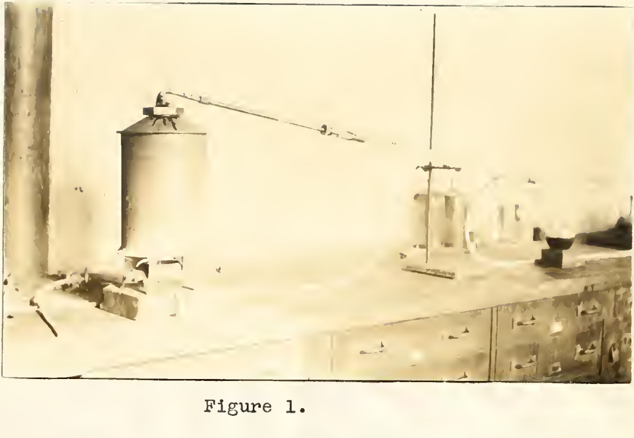

Figure 1.

First Primary Distillation.

In this distillation a sample of 4 liters was used. The following fractions were taken:

1st drop, at	89° C.
1st fraction	89-110° C.
2nd "	110-134° C.
3rd "	134-141° C.
4th "	141-150° C.
5th "	150-155° C.
6th "	155-160° C.
7th "	160-170° C.
8th "	170-180° C.
9th "	180-190° C.
10th "	190-200° C.
11th "	200-210° C.
12th "	210-250° C.
13th "	250-280° C.
14th "	290-320° C.
15th "	320-325° C.

These distillates even after treatment with Fuller's-earth had a very disagreeable odor.

Second Primary Distillation.

In a second primary distillation a sample of 4 liters was used. This sample weighed approximately 4½ pounds. The sample was treated with 10% by weight, or with 0.425 pounds of concentrated sulphuric acid in an attempt to obtain distillates which did not have a disagreeable odor. The mixture of drip oil and acid was agitated and then allowed to settle over night. In the morning, the upper liquid was drawn off from a considerable amount of the thick sludge at the bottom of the vessel. This sludge contained the impurities, and was discarded. The upper liquid was then introduced into the iron still and distilled, fractions being collected as follows:

1st drop at 93° C.

1st fraction	93-110° C. =	23 cc. =	0.57%
2nd "	110-130° C. =	88 cc. =	2.20%

3rd fraction 130 - 150° C. = 340 cc.= 8.5%

4th " 150 - 160° C. = 282 cc.= 7.05%

5th " 160 - 170° C. = 244 cc.= 6.10%

6th " 170 - 180° C. = 180 cc.= 4.50%

7th " 180 - 190° C. = 120 cc.= 3.00%

8th " 190 - 210° C. = 173 cc.= 4.33%

*9th " 210 - 249° C. = 500 cc.= 12.5%

10th " 248 - 260° C. = 148 cc.= 3.78%

11th " 260 - 300° C. = 360 cc.= 9.00%

12th " 300 - 320° C. = 172 cc.= 4.30%

13th " 320 - 335° C. = 558 cc.= 13.95%

14th " 335 -346 ° C. = 91 cc.= 2.28%

Residue of Coke.

*Approximately 500 cc., not measured because it contained a large amount of solid matter.

The distillates from this run had a strong odor of sulphur dioxide. In order to improve the odor and color of the distillates, they were treated with Fuller's-earth. The distillates were then subjected to fractional distillation.

Difficulties Encountered.

When a temperature of about 210° C. was reached the still head commenced to leak. An investigation showed that a solid had collected in the vapor neck. In order to overcome this difficulty we moved the condenser jacket as far as possible toward the end of the condenser tube, and packed the upper portion of the condenser tube with asbestos. In this way, the material in the tube was kept molten.

Fractional Distillation

*Theory:-

If the liquid is not a single substance, but a mixture, it is often possible to separate the constituents by a single distillation, provided the boiling points lie widely apart. The more volatile liquid first passes over, the temperature quickly rises, and the liquid of higher boiling point distils. It is otherwise when a liquid consists of substances boiling at temperatures not very far removed from one another, especially in the case of chemically related substances, such a constitute petroleum and coal-tar naphtha. One distillation suffices only to produce a very incomplete separation, a portion of the less volatile liquid being carried over in the first distillate, together with the more volatile body, the temperature gradually rising throughout the distillation.

In order to effect separation of the several substances, recourse is had to the method of fractional distillation. The liquid is distilled in a round flask, which is surmounted with a fractionating column, holding the thermometer.

The effect of the column may be explained as follows: The vapor given off from a mixture of liquids contains, as a rule, a larger proportion of the more volatile constituent than the liquid. If this vapor is partly condensed in its ascent, the vapor above this condensed liquid will be still richer in the more volatile constituent. If, by a series of constructions or diaphragms, the condensed liquid is obstructed in its return flow, a momentary equilibrium between liquid and vapor is established at each diaphragm, and the longer the column the greater will be the amount of the more volatile constituent in the last portion of

vapor to undergo condensation. This passes off by the condenser, and is collected in the receiver. By this means a partial separation is effected, and the portions distilling within a range of a small number of degrees are collected in separate flasks. Each of these portions or fractions is redistilled, and collected within still narrower limits of temperature, until at length the mixture is separated into certain portions, the boiling points of which are nearly constant, and these may be regarded as pure.

---

* J. B. Cohen, Theoretical Organic Chemistry.

Apparatus Used in Fractional Distillation.

The apparatus shown in figure 2, consists of a round bottom glass flask of 500 cc. capacity fitted with a medium sized Glinsky fractionating column. This column was fitted with a 400° C. thermometer and with a small glass condenser. The temperature registered on the thermometer was corrected for the thread of mercury which projected above the vessel. The distillates were collected in glass receivers.

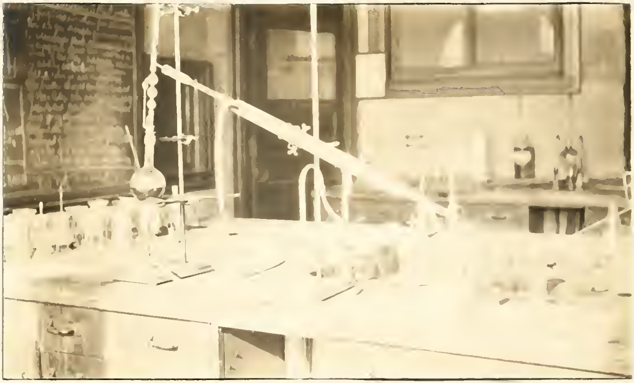

Figure 2.

Procedure.

The fractions from the first primary distillation were first subjected to fractional distillation and the fractions were collected at 10 degree intervals. The following fractions were collected:

up to 110°C, 110-120°, 120-130°, 130-140°, 140-150°, 150-160°, 160-170°, 170-180°, 180-190°, 190-210°, 210-250° (contained a large amount of solid material), 250-280° , 280-290°, 290-320°, 320-325°.

We were chiefly interested in the fractions whose boiling points were below 200°C. The fractions with boilings points below 190°C. were therefore redistilled and the distillation was carefully watched in order to determine the temperatures, as closely as possible, at which the maximum and minimum quantities of distillate

came over. The receivers were changed whenever a minimum point was reached. These fractions were distilled as follows:-

(A) The fractions, up to 110°C, 110-120°, 120-130° were united and redistilled, cuts being made as follows: up to 115° C, 115-124°, 124-127°, 127-130°.

(B) The fractions 130-140°C, 140-150°, were united, added to the residue from A and redistilled. The fractions were collected in the receivers used in the previous distillation and in addition the following cuts were made: 130-133°C, 133-137°, 137-144°.

(C) The fraction 150-160°C was added to the residue from (B) and redistilled. The fractions were collected in the receivers used in the previous distillations and in addition the following cuts were made: 144-150°C, 150-155°, 155-161°.

(D) The fraction 160-170°C. was added to the residue from (C) and redistilled. The fractions

were collected in the receivers used in the previous distillations and in addition a cut was made at 161-167°C.

(E) The fraction 170-180°C was added to the residue from (D) and redistilled. The fractions were collected in the receivers used in the previous distillations and in addition the following cuts were made: 167-172°C, 172-177°.

(F) The fraction 180-190°C. was added to the residue from (E) and redistilled. The fractions were collected in the receivers used in the previous distillations and in addition the following cuts were made: 177-184°C, 184-192°.

The fractions, up to 115°C, 115-124°, 124-127°, 127°-130°, 130-133°, 133-137°, 137-144°, 144-150°, 150-155°, 155-161°, 161-167°, 167-172°, 172-177°, 177-184°, 184-192°, were redistilled in a manner similar to that of the previous dis-

tillation and the fractions were collected in the same receivers. This process was repeated several times during an interval of more than three weeks. The residue remaining in the still at the end of several of the distillations solidified on cooling. These residues were set aside.

During this process of fractional distillation, we were unable to obtain fractions having constant boiling points, but owing to lack of time we were forced to discontinue the distillation. At the end of the distillation the fractions had the following volumes and the following approximate maximum points were noticed during the distillation:

Original Sample - 4000cc.

Fractions	volume	Per Cent.	Constant Points
up to 115°	60 cc.	1.5	112° C.
115-124	40	1.0	120
124-127	45	1.12	126
127-130	70	1.75	128

130-133	55	1.38	132
133-137	80	2.00	135
137-144	300	7.5	140
144-150	200	5.0	
150-155	50	1.25	152
155-161	45	1.12	158
161-167	120	3.0	
167-172	90	2.25	169
172-177	100	2.50	176
177-184	55	1.37	179
184-192	30	.75	188

The distillates obtained were in most cases colorless mobile liquids, resembling commercial xylol to a large extent both in appearance and odor. The higher boiling distillates were dark colored liquids.

Identification of the Hydrocarbons.

Investigation of Solids, both Residual and as Distillates, Obtained in the Primary and Fractional Distillations.

The solids obtained seemed to distil at about 190-250° C. and since naphthalene also distils within this range we suspected that this solid material might be naphthalene. This solid material did not have the characteristic naphthalene odor.

The solid was purified by pressing and then recrystallising it from hot alcohol. The purified body was filtered and then carefully dried. In this purified condition the solid material had the characteristic odor of naphthalene and also crystallized in shining plates resembling those of naphthalene.

The melting point of the purified crystals was now determined by means of the apparatus shown in figure (3). This apparatus consisted

of a Florence flask of about 500 cc. capacity about three quarters filled with concentrated sulphuric acid, a 0-360°C. thermometer to measure the temperature of the bath, a 0-100°C thermometer to measure the temperature of the stem of mercury which projected above the bath of sulphuric acid, and a capillary tube, sealed at one end, which contained a small quantity of the carefully dried, finely powdered substance. The finely powdered substance was introduced into the capillary to a depth of about 2 or 3 mm. The capillary tube was attached to the thermometer so that the substance was level with the bulb. The attachment was made by moistening the side of the capillary tube by contact with the thermometer bulb which has been dipped into the sulphuric acid. When pressed against the thermometer stem the capillary tube adhered. When a certain temperature is reached, the substance, if pure, melts suddenly within a range

of 1 or 2 degrees.

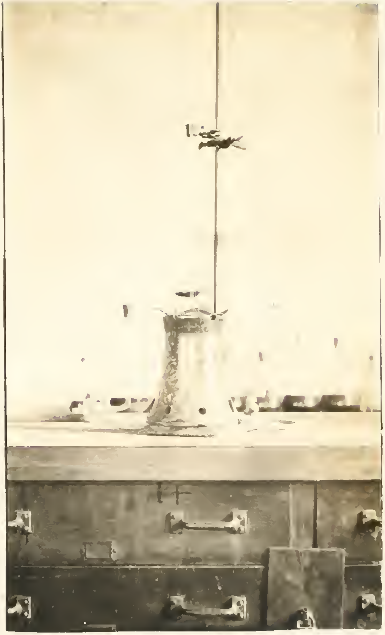

Figure 3.

The burner was lighted and the temperature was slowly raised. When the temperature reached 77.5°C. the substance started to melt and at 80.2°C the substance was entirely molten. The average temperature of melting was 78.8°C. The temperature of the correction thermometer was 44.2°C.

The correction for the portion of the thermometer stem which projects above the surface of the sulphuric acid is

$$N\ (T - t)\ 0.000154$$

where N is the length of the projecting column of mercury in degrees centigrade, T the temperature of melting, and t the temperature recorded by the correction thermometer at the temperature of melting.

The correction was

$90\ (78.8 - 44.2)\ 0.000154 = 0.5^{\circ}$ to be added.

The corrected melting point was

78.8 plus 8.5 = 79.3°C.

The correct melting point of naphthalene is 79.2°C. The melting point of the solid agrees with that of naphthalene, but this was not taken as sufficient proof, the trinitro body being later prepared.

The crystals from the fraction from the second crude distillation marked 210-249°C. were purified by pressing and crystallizing from hot alcohol. The melting point of these crystals was then determined.

The crystals started to melt at 78.5°C. and at 81.2°C they were entirely molten. The average temperature of melting was 79.8° C.

The correction temperature was 41°C. The correction for the portion of the stem above the surface of the liquid was

90(79.8 - 41) 0.000154 = 0.5° to be added.

The corrected melting point was

79.8 plus 0.5 = 80.2°C. which

checks very closely with the correct melting point of naphthalene.

Naphthalene is the only solid hydrocarbon, except pyrene and pseudophenanthrene, giving a precipitate when its cold alcoholic solution is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of yellow needles, melting at 149°C.

The trinitro derivatives of the two solids were prepared according to the preceding directions, and their melting points were determined.

The melting point of trinitro derivatives from the solid from the fractional distillation was taken.

Temperature of melting

148 - 150°C. - Average 149° C.

Correction temperature = 41°C.

Temperature correction

160 (149-41) 0.000154 = 2.6° to be added.

149 plus 2.6 = 151.6°C. corrected, melting point, which checks closely with that of the trinitro naphthalene.

The melting point of the trinitro derivative from the fraction marked 210-249°C was determined.

- Temperature of melting

146.5 - 149.5°C. - Average 148°C

Correction temperature = 71.5°C.

Temperature correction =

140 (148-71.5) 0.000154 = 1.6° to be added.

148 plus 1.6 = 149.6°, corrected melting point which checks closely with that of trinitro naphthalene.

Both the solid from the fractional distillation and that from the fraction marked 210-249° were the same. Since these solids have the same crystalline appearance and the same characteris-

tic odor as naphthalene and since the melting point of these crystals and the melting point of the trinitro derivative prepared therefrom is the same as that of naphthalene and that of the trinitro derivative of naphthalene this is conclusive evidence of the presence of naphthalene.

Investigation of Fraction
Marked 137-144°C.

The fraction marked 137-144°C. was suspected to contain the three xylenes. We attempted to prepare the meta and para trinitro xylenes by the following method:

Equal measures of fuming HNO_3 (sp.gr.1.5) and concentrated H_2SO_4 are mixed and allowed to cool. The operation is conducted in the cold. The hydrocarbon is gradually added and the product allowed to stand several hours. It is then poured into an excess of water, the liquid passed through a wet filter, the separated nitro-deriva-

tives recrystallized from boiling alcohol and examined under the microscope.

Trinitroparaxylene is much more soluble in hot alcohol than the isomeric meta xylene derivative and crystallizes in large colorless needles m. p. 137°C.

The trinitrometa xylene melts at 176°C. and crystallizes in thin, colorless, flattened needles.

Trinitro meta xylene yields nitro diamido meta xylene on partial reduction. Nitrodiamido meta xylene $C_6H(CH_3)_2(NH_2)_2NO_2$ is formed by the reduction of trinitro meta xylene with ammonium sulphide. It is slightly soluble in cold, more readily in boiling water and readily in alcohol from which it crystallizes in lustrous, ruby red prisms often an inch in length, which melt at 212-213°C.

We were able to prepare the meta and para trinitro xylenes but we were unable to separate them by fractional crystallization. We attempted to

prepare the nitro diamido meta xylene and obtained a dark red solution but were unable to obtain the lustrous ruby prisms.

Figure 4.

We next resorted to the use of the microscope, shown in figure 4. A sample of commercial xylol was secured and the meta and para trinitro xylenes prepared. We nitrated a portion of the fraction marked 137-144°C., in the same way. Each of these batches of crystals was dissolved in hot alcohol and allowed to crystallize on a glass plate. These crystals were examined under the microscope, using a low power objective and the crystals were identified as being the same. The presence of the meta and para xylenes was therefore confirmed.

The fraction 137-144°C is repeatedly shaken with concentrated H_2SO_4 and the ortho and meta xylenes alone are dissolved. The solution is diluted with water and neutralized with chalk, the filtrate being then treated with an excess of $Na_2\ CO_3$ and concentrated by evaporation. The sodium ortho xylene sulphonate separates out on

cooling in large prisms which can be purified by recrystallization. The meta xylene remains in solution. Sodium Ortho Xylene Sulphonate, $C_6H_2(CH_3)_2\ SO_3\ Na + 5H_2O$ crystallizes in flat prisms, the size of which seem to be limited only by the size of the vessel. These crystals effloresce in the air.

We prepared the Sodium Ortho Xylene Sulphonate according to the preceding method and obtained crystals which answered the description of the Sodium Ortho Xylene Sulphonate. From this evidence and from the fact that if the meta and para xylenes are present the ortho xylene is almost invariably present, we consider that we have shown sufficient evidence to prove the presence of the ortho xylene.

Investigation of the Fraction Marked 161-167°C.

Dinitro mesitylene, $C_6H(NO_2)_2\ (CH_3)_3$ is very readily formed when mesitylene is allowed to drop into well cooled, fuming nitric acid. The solution is poured into cold water after standing for some time and the curdy precipitate washed with water. It crystallizes from hot alcohol in colorless lustrous rhombic prisms, often an inch in length, which melt at 86°C.

"The extreme readiness with which mesitylene is completely converted in the cold into this splendid crystalline compound is so characteristic that it affords the best means of detecting the compound." (Fittig)

Trinitro mesitylene is obtained similarly - using 1 volume of fuming HNO_3 and 2 volumes of concentrated H_2SO_4. It is insoluble in cold alcohol and slightly soluble in hot alcohol from which it crystallizes in white fine needles, which

melt at 230-232°C. It separates from hot acetone in which it is more readily soluble in transparent vitreous prisms belonging to the assymmetric system.

We set out to prepare the dinitro mesitylene but obtained the trinitro mesitylene instead, owing to the difficulty of controlling the nitration. The melting point of these crystals was found to agree very closely with the melting point of the trinitro mesitylene. We therefore determined the presence of mesitylene.

We attempted to prove the presence of Pseudocumene, Cymene, and Ethyl Benzene, but we were unsuccessful both because of lack of time and the difficulty of obtaining a pure body.

Conclusion.

As a result of our investigation, we found that drip oil consists chiefly of a mixture of liquid, aromatic hydrocarbons having boiling points which lie very close together; for example, ortho-xylene, b.p. 142°C; metaxylene b.p. 139°C, and paraxylene b.p. 138°C., were found to be present. The presence of mesitylene, (trimethyl benzene), the higher homologue of xylene, (dimethyl benzene) was also confirmed. The only solid hydrocarbon found was naphthalene and this was found in large quantities in the fraction 190-250°C. No paraffins were found. The results obtained were only qualitative.

Bibliography.

A. W. Titherley:
A laboratory course of Organic Chemistry.

Neave and Heilbron:
The identification of organic compounds.

Mulliken:
Identification of Pure Organic Compounds.

J. B. Cohen:
Practical Organic Chemistry.
Theoretical Organic Chemistry.

Roscoe and Schorlemmer:
Treatise on Chemistry Parts III, IV and V.

Miller:
Elements of Chemistry Part III.

Allen:
Commercial Organic Analysis Vol. 3.

Lunge and Keane:
Technical Chemical Analysis.

Young:
Fractional Distillation.